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Environmental Fate of Picloram Used for Roadside Weed Control

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ABSTRACT

The herbicide picloram (4-amino-3,5,6- trichloro-2-pyridine carboxylic acid) was applied to control spotted knapweed (*Centaurea maculosa* Lam.) in the northern Rockies to determine persistence in soils and vegetation, losses by photodegradation, rainfall induced migration, and potential contamination of surface and groundwater. Two sites were selected to represent best case and worst case conditions (within label restrictions) for on-site retention of picloram. A valley bottom terrace was treated with 0.28 kg/ha of picloram in the spring of 1985, and sampled over the following 445 d. In the spring of 1986, 1.12 kg/ha of picloram was applied to both sides of a minimal construction logging road extending 4 km along a stream (102 to 815 m^3) that drains a granitic upper mountain watershed. Of the 17.1 km^2 watershed, 0.15% (2.5 ha) was sprayed. Vegetation, soils, surface water, and groundwater near the road were sampled during the 90 d following application. At the valley bottom site, 36, 13, and 10.5% of the picloram applied persisted after 90, 365, and 445 d, respectively. At the mountain watershed site, 78% persisted after 90 d, and picloram was not detected in the surface or groundwaters during the 90 d following application. Depending on the timing of delivery, as little as 1% or less of the application could have been detected after delivery to the stream. Loss by photodegradation during the first 7 d after treatment was important at both sites.

LACEY (1983) estimated that spotted knapweed has spread at a rate of 27% per yr in the northern Rocky Mountains. By 1986, this nonnative occupied 2 million ha in Montana, and another 2 million in adjacent states and Canadian provinces, reducing forage for livestock and wildlife. Land managers are using herbicides to slow the spread in anticipation of establishing biological control agents. Roadsides are a primary invasion route, so current control programs involve extensive roadside spraying with picloram that is also used on other *Centaurea* species, leafy spurge (*Euphorbia esula* L.), and brush.

The widely used K salt of picloram is highly water soluble and relatively persistent in soil (Norris, 1970; Bovey and Scifres, 1971). Practical application rates range from 0.28 to 9.0 kg/ha acid equivalent (ae). Soil residues above 1 to 10 μg/kg have been detected for 60 d to 6.6 yr (Johnsen, 1980; Keys and Friesen, 1968; Marley, 1980; Fryer et al., 1979; Sirons et al., 1977; Bovey et al., 1974, 1975; Davis and Ingebo, 1973). Decay in soils is primarily biological (Hance, 1967), so warm, moist climates with high microbial activity enhance decay while cool, dry conditions prolong persistence (Davis and Ingebo, 1973; Hamaker et al., 1967).

Picloram follows the movement of water in an ecosystem (Bovey and Scifres, 1971) because of its high water solubility (more than 400 000 g/m^3 at 25 °C for the K salt, according to Neary et al., 1985). Reassociation in the soil to the acid form (pKa 3.6) still maintains a solubility of 430 g/m^3 (WSSA, 1983). Picloram is held in soil primarily by adsorption to organic matter (Grover, 1971; Farmer and Aochi, 1974; Davidson and Chang, 1972). Leaching of picloram in soil increases with higher sand content (Merkle et al, 1966; Scifres et al., 1969; Baur et al., 1972; Herr et al., 1966a) and a higher macropore to micropore ratio (Davidson and Chang, 1972; Rao et al., 1974; Ping et al., 1975). From <1 to 6% of applied picloram was observed to move from treated areas into drainage channels (Neary et al., 1985; Mayeux et al., 1984; Johnsen, 1980; Trichell et al., 1968).

Potential for significant movement from treated sites exists in the northern Rockies. Treatment often occurs in spring (during rapid plant growth to maximize control) just before maximum runoff from snowmelt and spring rains. Mountain soils are shallow, sandy, and coarse with little organic content. Mountain roads were often constructed on steep slopes, near and parallel to streams or intermittent drainages. Road construction enhances runoff by concentrating flows on compacted road surfaces and ditches, intersecting groundwater flow at the cut slope, and using coarse material, low in organic matter, to create the fill slope. Streams near roads may be at risk for significant contamination by picloram.

Reported LC_{50}'s (lethal concentration for 50% of the organisms) for fish are >4250 mg/m^3 (Woodward, 1976; Kenaga, 1969). Based on a 22-d flow-through bioassay on cutthroat trout (*Salmo* spp.) Woodward (1979) suggested that instream concentrations not be allowed to exceed 290 mg/m^3. Picloram does not accumulate in fish tissue in concentrations above that of the surrounding water (Youngson and Meikle, 1972, unpublished data).

Much stream runoff in the northern Rockies irrigates alfalfa (*Medicago sativa* L.), a crop particularly sensitive to picloram (Herr et al., 1966b; Marley, 1980). Bovey and Scifres (1971) suggest that growth of sensitive crops would not be affected by a single watering at 1 to 4 mg/m^3, but repeated waterings at 4 mg/m^3 could reduce growth, and 10 mg/m^3 in irrigation water could severely affect growth. Toxicity of picloram to mammals is low and residues are rapidly excreted in urine and feces (Kutschinski and Riley, 1969). The National Research Council (1983) recommended a chronic SNARL (suggested no adverse response level) of 1050 mg/m^3 for drinking water.

This study follows the dissipation of picloram over time in several ecosystem compartments. We determined picloram loss by photodegradation on vegetation and soil, its leaching in soil as affected by rain, and loss to surface and groundwater.

MATERIALS AND METHODS

Two sites representing very different environmental conditions were selected (Table 1). A valley bottom terrace maximized retention of picloram and allowed evaluation of per-

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Table 1. Contrasting characteristics of the two study sites.

Site	Fort Missoula	North Fork, Elk Creek
Type	Valley bottom field	Mountain watershed with logging road by stream
Application rate	0.28 kg/ha	1.12 kg/ha
Soil texture	Loam	Sandy loam
Percent sand	33%	61%
Organic matter	20–40 g/kg	8–20 g/kg
Depth to C horizon	81–147 cm	20–50 cm
Depth to groundwater	10 m	0.9–2.7 m
Distance to surface water	500 m	Shortest distance 1 m Average distance 33 m
Slope	<1%	6%
Vegetation	Old field	Douglas fir, snowberry, pinegrass, bluebunch wheatgrass
Application date	18 June 1985	6 June 1986

sistence under relatively dry conditions. The second site was a minimal construction logging road adjacent to a stream draining a small, granitic mountain watershed. It provided potential movement of picloram into ground and surface water and permitted estimation of a watershed budget for any transported picloram.

Site Description And Treatment

The Fort Missoula site (46° 50′ 45″ N, 114° 3′ 50″ W) is a valley bottom terrace in an intermountain valley at 960 m near Missoula, MT. Average annual precipitation and air temperature are 338 mm and 6.7 °C with 105 to 120 frost-free d.

The deep, well-drained alluvial soil is a coarse, silty, mixed, frigid Calciorthidic Haploxeroll (DeSmet series) of <1% slope. The surface horizons have been disturbed so that the Ap and part of the Bw horizons are mixed to 50 cm deep. These horizons have a loam texture with 12% coarse material (0.2–2.0 cm) and an estimated 20 to 40 g/kg organic matter content. Bulk density is 1.22 g/cm^3, and pH is neutral to mildly alkaline as depth increases. Extending to 66 to 106 cm, the Bw horizon is a strongly effervescent, moderately alkaline, fine sandy loam with up to 10% pebbles, some cobbles, and soft masses of lime. Extending to 81 to 147 cm, the Bk horizon is a silt loam or very fine sandy loam with a Ca content of 120 g/kg. Below it, the 2C horizon is a fine sandy loam with many pebbles and cobbles. Permeability is moderate (1.5–5.1 cm/h) through the Ap and B horizons then rapid (15.2–50.8 cm/h) below. The groundwater table was estimated at 10 m.

When treated, the vegetative cover was 9% grasses (six species), 39% spotted knapweed, and <1% other, primarily weedy, forbs (13 species). Bare ground was 44%. Biomass as dry weight of live and standing dead vegetation was 784 kg/ha.

An exclosure was divided into four 30- by 20-m treatment plots. A grid of square meter subplots was superimposed on the exclosure, permitting selection of sampling points by random number. A 2-m buffer zone surrounded each treatment.

On 18 June 1985, the K salt of picloram (Tordon 22K Trademark, Dow Chemical Co., Walnut Creek, CA) was sprayed on two plots by truck at 0.28 kg/ha a.e. Two plots were not sprayed. Wind speed averaged 4.5 km/h, with a maximum of 9.6 km/h. Nalco-Trol (Nalco Chemical Co., Chicago, IL), a drift retardant and deposition aid was used at 12 mL/100 L.

The North Fork of Elk Creek (46° 51′30″ N, 113° 18′ W) is 55 km east of Missoula, MT. The site is a minimal construction logging road adjacent to a stream draining a small, granitic, mountain watershed (17 km^2). Average distance from the road edge to the stream is 33.5 m, with the stream immediately adjacent in some areas. Elevation rises from 1265 to 1435 m over the 4 km of treated road. At 1280 m, average annual precipitation and temperature are 406 mm and 5 °C.

Soils (Ambrant-Rock Outcrop Associations) are shallow sandy loams of variable depth, formed from granite colluvium, with numerous granitic outcrops. The sandy texture (61% sand) results in moderately rapid permeability (5 to 15 cm/h) and low available water capacity. The coarse fraction (0.2–2.0 cm) averages 22.5%. Bulk density is 1.65 to 1.70 g/cm^3, and pH is 8 throughout the profile. Organic matter in the first meter is 8 to 20 g/kg except for small areas where the forest canopy has enriched the top 4 cm to 60 g/kg. The B horizons are lacking, and the C horizon is at 20 to 50 cm.

The vegetation alternates between meadows, shrub thickets, and forest, and is dominated by Douglas fir [*Pseudotsuga menziesii* (Mirbel) Franco], snowberry [*Symphoricarpos albus* (L.) Blake], and pinegrass (*Calamagrostis rubescens* Buckl.) or bluebunch wheatgrass [*Agropyron spicatum* (Pursh) Scribn. and Smith]. Before treatment, biomass averaged 3322 kg/ha of live and standing dead plants <1 cm in diam. and 1 m high.

The spray swath was 3.3 m wide on either side of the road. Both sides of the 4-km road were divided into 99 increments (198 subplots, 40 by 3.3 m). Subplots and sampling points were chosen by random numbers.

On 6 June, 1986, picloram was applied at 1.12 kg/ha (a.e.) to both roadsides using offset spray nozzles supplemented by a hand gun where the cut slope blocked spray. Wind gusts ranged from 3 to 13 km/h during the 65-min application. Nalco-Trol was used at 12 mL/100 L spray solution. Both sites were treated by Missoula County Weed Control following EPA label restrictions.

Sampling Procedures

Samples were collected the day before application, the day of application (Day 0), and 7 and 90 d after. Fort Missoula was also sampled after 365 and 445 d. Duplicate field samples were collected for each type of sample by compositing 30 or 60 subsamples from 30 randomly chosen subplots.

The application rate was measured using deposition on 9-cm petri dishes containing 80 g of laboratory grade silica sand. Two dishes were placed in each of 60 random subplots. One member of each pair was collected immediately after spraying. Half of these were composited to produce one field duplicate and half for the other. The second dish of the pairs was collected 7 d after spraying to estimate photodegradation at the soil surface.

Vegetation for picloram and biomass analysis was collected by clipping all standing live and dead plant material up to 1-cm diam. and 1-m high in a 20- by 50-cm quadrat in 30 randomly chosen subplots. Cover class was estimated using the Daubenmire method.

Soils were sampled at 0 to 12.5 cm, 12.5 to 25 cm, 25 to 50 cm, 50 to 75 cm, and 75 to 100 cm deep. At Fort Missoula, only the surface layer was sampled on Days 0 and 7 since no rain had occurred to leach the picloram. A two stage coring procedure was used to minimize contamination of deeper strata by soil from upper strata. The subsample for each stratum was first collected with a 2.3-cm diam. coring tube; then an 8.3-cm diam. bucket auger was used to enlarge the hole down to the top of the next lower stratum before the smaller coring tube was used to collect the lower stratum. Sampling equipment was cleaned between samples.

At the mouth of the North Fork, a continuous water level recorder in a stilling well and a 152-cm Parshall Flume measured discharge from 4 June to 4 Sept. 1986. At both sites rainfall was measured during the first 90 d after spraying. Subsequent rain data for Fort Missoula and daily sunlight period were obtained from a permanent weather station 8 km northwest.

Surface water samples were collected on 4 June 1986 to determine background levels and to create standards and blanks. During application, duplicate subsamples were taken every 6 min for 48 min when water potentially contaminated from drift would be expected to pass the sampling point.

Surface water samples were collected every 3 d during base flow for the first 30 d after application, then weekly for another 30 d. No detectable picloram was found in any base flow samples, hence base flow sampling ceased until Day 90. The stream was sampled every 3 h during rising and falling hydrographs associated with rain events. Duplicate grab samples were taken from the flume mixing zone. The application began adjacent to the stream directly above the flume.

Shallow groundwater wells were hand-augered in the unsprayed zone between road and stream. Nine wells were arrayed in three nests of three wells each. A 10th was placed within the sprayed swath on the stream side of the road. The depth of these sampling wells varied from 2.1 to 3.7 m with depth to groundwater varying from 0.9 to 2.3 m on Day 0 (4 June 1986). The water table dropped throughout the sampling period.

The wells were cased using 3.8-cm i.d. PVC pipe with 1-mm slot PVC sand point well screens. The space around the casing was backfilled with well cuttings to the top of the water table then sealed with bentonite. Teflon tubing extended to the bottom casings through rubber well caps. A vacuum pump drew groundwater directly into sampling jars. Stagnant water was evacuated from wells 8 to 24 h before sampling. Wells were covered during application.

Two duplicate groundwater samples were formed each sampling day by randomly compositing subsamples from the wells between road and stream. Samples from the well located in the spray swath were analyzed separately. Groundwater was sampled prior to application, on Day 2 (first rain event after application), Day 7, and Day 90.

Water samples were collected in foil-covered glass jars, adjusted to pH 11 with NaOH, transported on ice, then held at 4 °C. Sand, soil, and vegetation samples were composited into foil-covered glass jars, transported on ice, then stored frozen. All equipment and glassware were cleaned with lab detergent and hot tap water, rinsed with hexane and then deionized water.

Sample Processing

Processing was conducted in subdued light. Sand and soil were air-dried in the dark, passed through a 2-mm sieve, mixed and split using a rift type sample splitter. Vegetation was chopped wet into 0.5-cm pieces, remixed but not dried. Aliquots for analysis were placed in foil-covered glass jars with foil-lined lids. Aliquots not used for analysis were dried to constant weight to provide a moisture correction.

Picloram Analysis

The 1985 samples were analyzed following the Oregon State Agricultural Laboratory adaptation of Anonymous (1972). Samples were treated with 1 *M* NaOH, acidified to pH <3, and extracted with ethyl ether. Borontriflouride in methanol was used for esterification of the extract. Picloram was extracted from water by ethyl ether at pH <2.2, the extract evaporated in the presence of KOH to hydrolyze all forms to the K salt, acidified to the acid, and the methyl ester formed with borontrifluoride (Anonymous, 1978). Extract analysis was on a Perkin Elmer Model 3920 gas chromatograph with an electron capture detector. The first analysis used a column packed with 3% OV17 on Gaschrom Q (diatomaceous earth treated with dichlorodimethyl silane) at 230 °C. Positive samples were confirmed on a second column at 190 °C packed with 5% QF1 + 3% DC200 on Gaschrom Q.

The second year of study (1986), soil and sand were extracted following Bjerke (1973), vegetation following Anonymous (1977), and water according to Anonymous (1978). Analysis was on a Hewlett-Packard 5730A with the primary column packed with 3% OV225 and held at 220 °C, and the confirmatory column packed with 3% SP2100 at 190 °C.

Agreement between the two methods was quantified by recovery of blind spikes (see QC/QA section) and was acceptable for this study.

Statistical Design

Fifty-six environmental compartment/time periods were measured. The high cost of analysis precluded statistical designs dependent on large numbers of replicate samples to estimate standard errors. Precision was instead quantified by duplicate sample agreement percent (DSA%) between replicates.

$$DSA(\%) = [d1/(d1 + d2)/2] \times 100\%$$

where d1 is the lower of the duplicate values.

Representativeness of field samples for picloram residues was obtained by random selection of subplot locations and by subsample sizes of 30 to 60. Compositing this many subsamples was assumed sufficient to reach the asymptotic portion of the student's *t* distribution.

Quality Control/Quality Assurance (QC/QA)

Precision was quantified by DSA% at four steps in the process: field sampling duplicates, processing duplicates from the same sample, duplicate extractions from the same sample, and duplicate injections of the same extraction. The first two types of duplicates were submitted as blinds to the analytical lab.

Analytical recovery for each analytic run was estimated from fortified samples (spikes) created both by the analytical lab and by the authors (submitted as blinds to the lab). Fortified samples were made by adding known amounts of picloram standard to silica sand and to soil, water, and vegetation collected before the application. Reagent blanks, field scour blanks, and processing rinse blanks were analyzed.

The analytical lab made duplicate injections of the same extraction and duplicate extractions of the same sample. The DSA's exceeded 94% agreement with standard deviations below 6% (Table 2). The mean DSA's for blinds were in

Table 2. Quality assurance data [mean ± standard deviation (sample size)].†

	Duplicate sample agreement, %					Analytic recovery, %	
Type	Injections	Extractions	Blind spikes	Blind splits	Blind field	Lab spikes	Blind spikes
Sand	94 ± 5.5(8)	94 ± 0.7(2)	94 ± 2.1(2)	86 ± 9.3(6)	90 ± 4.8(4)	108 ± 12 (4)	77 ± 23(4)
Soil	98 ± 3.9(8)	98 ± 2.9(5)	94 ± 5.1(4)	84 ± 15(18)	88 ± 13(28)	84 ± 7.6(5)	67 ± 27(10)
Veg	99 ± 0.6(4)	98 ± 1.3(5)	81 ± 11 (4)	89 ± 13(10)	90 ± 8.4(10)	83 ± 13 (5)	57 ± 23(7)
Water	99 ± 0.4(4)	100 ± 0 (5)‡	91 ± 4.6(5)	NA	60 ± 54(6)§	86 ± 5.2(6)	96 ± 47(15)¶
					100 ± 0 (6)§		79 ± 12(13)¶

† NA = not applicable.

‡ All five duplicate extractions were made on water samples with no detectable picloram.

§ During one analytic run several false positives of about 2 mg/m³ were recorded resulting in calculated duplicate sample agreements (DSAs) of 0%; however, reanalysis indicated values below detection, causing DSAs to approach 100%.

¶ During one analytic run the recorded values for two blind spikes resulted in recoveries of 243% and 163%; all other recoveries were <100%.

excess of 80% with standard deviations of 15% or less (with one exception). There was no dominant source of imprecision in the sampling, processing, and analytic methods.

A mean DSA of 60 ± 54% for blind field duplicates of water samples included two false positives that were reanalyzed and confirmed to be below detection. Without these, the DSA approached 100%.

Mean recoveries from spikes made by the analytic lab ranged from 84% for vegetation to 108% for sand. Recoveries from blind spikes were lower and associated standard deviations higher. For analytic runs with a large discrepancy between lab spike recoveries and those based on blind spikes, blind spikes were used to correct unknowns for analytic recovery. When lab and blind spikes agreed, their average recoveries were used. Concentrations presented here were corrected for recovery.

Minimum detection levels were 0.5 mg/m^3 for water, usually 5 or 6 μg/kg for soils and sand, occasionally as high as 20 μg/kg for soil. Minimum detection levels were usually 10 μg/kg for vegetation but as high as 350 μg/kg in 1985.

Soil concentrations apply to the size fraction passing a 2-mm sieve. To convert soil concentrations to pools (kg/ha) for bulk soils, corrections were made for bulk density and the fraction >2 mm for each stratum.

Dissipation rates were summarized as rate constants (k_s) using the first order equation:

$$k_s = [\ln(P_t/P_o)]/t$$

where P_o is the initial pool of picloram, P_t is the pool at some later time t, t is the interval in days. Although half-order kinetics are recommended for the description of picloram dissipation at some concentrations, first order kinetics are considered appropriate for the levels observed in this study (Hamaker et al., 1967; Youngson et al., 1967; Grover, 1967).

RESULTS AND DISCUSSION

Concentrations are presented (Tables 3 and 5) for assessing possible biotic effects of picloram. Concentrations, vegetation weights, and soil bulk densities were used to calculate picloram pools (Tables 4 and 6). The total pool measured on Day 0 was set equal to 100%, and portions of this initial pool that moved into other compartments and persisted over time are also presented in Tables 4 and 6.

Fort Missoula Site

The history of the Fort Missoula site indicates no previous treatment with picloram, and none was detected in the prespray samples (Table 3). Soil samples taken from adjacent untreated plots immediately after application were also below detection, indicating that drift was not significant.

Picloram was limited to the upper 12.5 cm of soil on both Day 0 at 151 μg/kg and Day 7 at 88 μg/kg (Table 3). On Day 90 the picloram concentrations were 23, 22, and 7 μg/kg in the first through third strata. By Day 365 the first stratum had declined to 12 μg/kg, the second to 11 μg/kg, and concentrations in deeper strata were below detection (<6 μg/kg). Surface soil residue was sufficient to kill knapweed seedlings in 1986. Two years after treatment (1987), soil residues had dropped below the toxicity level for knapweed that was becoming reestablished on the treated plots.

On the day of application the vegetation canopy intercepted enough picloram to produce a concentration of 32 300 μg/kg (Table 3). This was within the range to be expected following a 0.28 kg/ha application (Scifres et al., 1971a; Getzendaner et al., 1969; Bovey et al., 1974). The concentration declined to 5040 μg/kg by fall. The second season's growth apparently absorbed enough picloram from the soil to reach concentrations of 1310 to 882 μg/kg. Concentrations measured from Day 90 to Day 445 were higher than might be expected from other studies. Bovey et al. (1967) recognized root uptake from the soil but did not consider it significant in Texas with its higher soil decay rates.

Using concentrations to calculate pools, deposition to sand, soil, and vegetation was estimated to be 0.243, 0.231, and 0.025 kg/ha, respectively (Table 4). Measured deposition on soil plus vegetation accounted for 91% of the intended application (0.28 kg/ha).

Loss rates from all pools from Day 0 to Day 7 can be attributed largely to photodegradation. Soil-water content at Fort Missoula at the time of spraying was <5%. There was no rainfall at the site until Day 45 except for a 0.75-mm precipitation event on Day 2. Lack of rain and low soil-water content prevented leaching and limited both microbial decay and plant growth and uptake. Standing crop increased by only 19 kg/ha (2%) from Day 0 to 7 as vegetation entered dormancy induced by summer drought.

As calculated from the initial depositions listed in Table 4, loss rates for Day 0 to Day 7 have exponential rate constants attributable to photodegradation of 0.23 on sand, 0.16 on vegetation, and 0.077 on soil. For the total system (soil plus vegetation), the loss rate was 0.083.

The loss rate in sand should be a better measure of photodegradation than is that of soil since sand is low or lacking in organic matter, moisture, and microbial populations. The higher loss rate on sand relative to

Table 3. Picloram concentrations (μg/kg) in environmental compartments at Fort Missoula with an intended application of 0.28 kg/ha.†

	Prespray†	Day 0	Day 7	Day 90	Day 365	Day 445
Sand	NA	1 888	381	NA	NA	NA
Vegetation	<MDL 100	32 300	9 610	5 040	1 310	882
Soil strata 1 (0–12.5 cm)	<MDL 20	151	88	23	12	11
Soil strata 2 (12.5–25 cm)	<MDL 20	NS	NS	22	11	8
Soil strata 3 (25–50 cm)	<MDL 20	NS	NS	7	<MDL 6	<MDL 5
Soil strata 4 (50–75 cm)	<MDL 10	NS	NS	<MDL 5	<MDL 6	NS
Soil strata 5 (75–100 cm)	<MDL 10	NS	NS	<MDL 5	<MDL 6	NS
Untreated plots	NA	<MDL 20	NS	NS	NS	NS

† NS = not sampled, no herbicide anticipated; NA = not applicable. <MDL = picloram was not detected at the listed minimum detection level.

Table 4. Picloram (kg/ha) in environmental compartments following an intended application of 0.28 kg/ha on the Fort Missoula site.†

	Day 0	Day 7	Day 90	Day 365	Day 445
Sand	0.243	0.049	NA	NA	NA
Vegetation	0.025 (10%)	0.008 (3%)	0.002 (1%)	0.002 (1%)	0.002 (1%)
Soil strata 1 (0–12.5 cm)	0.231 (90%)	0.135 (53%)	0.035 (14%)	0.016 (6%)	0.015 (6%)
Soil strata 2 (12.5–25 cm)	NS	NS	0.034 (13%)	0.016 (6%)	0.010 (4%)
Soil strata 3 (25–50 cm)	NS	NS	0.020 (8%)	ND	ND
Soil strata 4 (50–75 cm)	NS	NS	ND	ND	NS
Soil strata 5 (75–100 cm)	NS	NS	ND	ND	NS
Soil totals	0.231 (90%)	0.135 (53%)	0.089 (35%)	0.032 (12%)	0.025 (10%)
Soil + veg	0.256 (100%)	0.143 (56%)	0.091 (36%)	0.034 (13%)	0.027 (11%)
Precipitation cumulative, mm		<1	172	431	529

† NS = not sampled, no herbicide anticipated; ND = picloram was not detected. Percentages are the percent of the initial application persisting in each compartment.

soil likely results from less shading of the petri dishes that displaced the canopy slightly.

Following a 15.5-mm rainfall on Day 45, losses were caused by a combination of processes (photodegradation, microbial decay, foliar washoff, translocation, leaf drop, and soil leaching). During the 1985 growing season, the soil moisture wetting front advanced to a depth of 61 to 76 cm by Day 89 (cumulative rainfall through Day 90 was 172 mm). Picloram was never detected below 50 cm. After 1 yr and 431 mm of precipitation, detectable picloram was limited to the first 25 cm.

The plant canopy intercepted 9.8% of the initial measured application that rapidly photodecayed to one-third of the Day 0 pool by Day 7. The site received 171 mm of rain between Day 45 and 90, which was sufficient to break dormancy induced by summer drought and initiate fall growth of picloram resistant grasses. Picloram leached into soil may have been absorbed by roots and translocated to new growth (Scifres et al., 1971b), partially compensating for continuing photodegradation and foliar washoff. Although concentrations in vegetation continued to decline, the pool of picloram in vegetation was maintained at 0.002 kg/ha on Days 90, 365, and 445 due to root uptake and increases in biomass. More favorable moisture conditions during spring 1986 allowed biomass on treated plots to increase threefold from 784 kg/ha in the first growing season to 2247 kg/ha on Day 365 (2004 kg/ha on Day 445). Second season biomass was 91% grass, which had replaced knapweed.

One year after application, 13% of the initial deposition of 0.256 kg/ha was still present, mostly in soil where it was leached by late summer rains in 1985 (Table 4). Four hundred forty-five days after application, 10.5% persisted, almost all of this in soil.

Slope was <1% and the wetting front never exceeded 1 m, so there was no surface runoff nor leaching losses. Except for minor removals by rodents and insects, all losses represent in-place breakdown.

The rate of loss from all compartments declined with time. Assuming that loss from the entire system (soil plus vegetation) follows first order kinetics, loss rate constants fell from 0.083, when evaluated from Day 0 to 7, to 0.011 from Day 0 to 90. This declining rate of loss leveled off at 0.005 during the second year.

North Fork of Elk Creek Site

Analyses of prespray samples confirmed that the mountain watershed site was without detectable picloram residues (Table 5). Picloram was not detected in surface water samples collected during site treatment, indicating that spray drift into the stream was not measurable.

Picloram was limited to the top 12.5 cm of soil on Day 0 at 366 μg/kg (Table 5). The maximum concentration on Day 7 was 284 μg/kg from 0 to 12.5 cm and declined with depth to 21 μg/kg at 75 to 100 cm. Surface soil concentration continued to decline through Day 90, but leaching increased concentrations at some depths.

The plant canopy concentration was 166 000 μg/kg on Day 0 (Table 5), which is within the range to be expected following a 1.12 kg/ha application (Getzendaner et al., 1969). This initial concentration exceeded the EPA tolerance level of 80 000 μg/kg in forage grasses for livestock (Anonymous, 1987). By Day 7 vegetation levels had declined to 54 400 μg/kg and to 27 900 μg/kg by Day 90.

Picloram pools (kg/ha) estimated from these concentrations (Table 6) suggest initial depositions to sand, soil, and vegetation of 0.829, 0.625, and 0.552 kg/ha, respectively. Measured deposition to soil plus vegetation (1.177 kg/ha) was 105% of the intended application of 1.12 kg/ha.

From Day 0 to 7, picloram in sand declined at an exponential decay rate of 0.11 (Table 5) compared to the Fort Missoula decay rate of 0.23 (Table 3). Light exposure at the two sites differed greatly. The North Fork had a denser plant canopy, including an overstory of shrubs and trees, and a 3-mm rainfall event on Day 2 carried some picloram into the sand and soil. Photodecay increases with exposure time and with altitude because of increased ultraviolet (UV) light intensity (Hall et al., 1968; Johnsen and Martin, 1983). Exposure time and canopy shading were probably more important than altitude difference between these sites. In 1986 (the year of the North Fork study), 23 h of sunshine were recorded until the Day 2 precipitation event and 94 h through Day 7. In 1985 (first year of the Fort Missoula study), 114 h of sunshine were recorded through Day 7 without sufficient rain to leach picloram into soil or sand.

Table 5. Picloram concentrations (μg/kg) in environmental compartments at the North Fork of Elk Creek site with an intended application of 1.12 kg/ha.†

	Prespray	Day 0	Day 7	Day 90
Sand	NA	6 450	3 020	NA
Vegetation	<MDL 10	166 000	54 400	27 900
Soil strata 1 (0–12.5 cm)	<MDL 6	366	284	205
Soil strata 2 (12.5–25 cm)	<MDL 5	NS	70	94
Soil strata 3 (25–50 cm)	NS	NS	28	20
Soil strata 4 (50–75 cm)	NS	NS	22	22
Soil strata 5 (75–100 cm)	NS	NS	21	24
Ground-water	<MDL 0.5	NS	<MDL 0.5	<MDL 0.5
Surface water	<MDL 0.5	<MDL 0.5	<MDL 0.5	<MDL 0.5

† NS = not sampled, no herbicide anticipated; NA = not applicable. <MDL = picloram was not detected at the listed detection level.

Table 6. Picloram (kg/ha) in environmental compartments at the North Fork site following an intended application of 1.12 kg/ha.†

	Day 0	Day 7	Day 90
Sand	0.829	0.389	NA
Vegetation	0.552 (47%)	0.178 (15%)	0.084 (7%)
Soil strata 1 (0–12.5 cm)	0.625 (53%)	0.483 (41%)	0.437 (37%)
Soil strata 2 (12.5–25 cm)	NS	0.120 (10%)	0.167 (14%)
Soil strata 3 (25–50 cm)	NS	0.088 (8%)	0.070 (6%)
Soil strata 4 (50–75 cm)	NS	0.074 (6%)	0.078 (7%)
Soil strata 5 (75–100 cm)	NS	0.064 (5%)	0.081 (7%)
Soil Totals	0.625 (53%)	0.829 (70%)	0.833 (71%)
Soil + veg	1.177(100%)	1.007 (86%)	0.917 (78%)
Precipitation cumulative, mm		3	66

† NS = not sampled, no herbicide anticipated. Percentages are portion of the initial application persisting in that compartment.

Vegetation contained 47% of the initial pool applied at this site and only 10% of the initial pool at Fort Missoula. The higher interception by vegetation at the North Fork was a result of its higher leaf area index. Compared to 780 kg/ha at Fort Missoula, biomass at the North Fork site was 3300 kg/ha on Day 0, and included shrubs, lower tree limbs (<1-cm diam.) and accumulated dead grass. Merkle et al. (1966) reported 75 to 90% herbicide interception by heavy shrub cover.

Five hours before application, a 17-mm rainstorm saturated soils already charged by snowmelt. A 3-mm rainfall of Day 2 caused leaf drip and soil infiltration. Although no additional rain fell until Day 8, picloram had leached to the maximum sampled depth of 100 cm by Day 7.

Picloram declined most rapidly on vegetation, dropping by Day 7 to a third of the 0.552 kg/ha measured on Day 0, an exponential loss rate of 0.16. The Day 0 soil pool (0.625 kg/ha) increased by a third by Day 7 as a result of the 3-mm rainfall on Day 2, washing picloram off vegetation. From Day 7 to Day 90, the soil pool remained constant with some downward displacement. The exponential decay rate for soil plus vegetation through Day 7 was 0.022, considerably lower than the 0.083 loss rate observed at Fort Missoula.

After 1 wk, 86% of the initial measured deposition (Table 6) was still present at the North Fork (70% in soil). After 90 d, 78% of the initial application persisted (71% in soil). Persistence at Fort Missoula had been 56% after 1 wk and 36% after 90 d. This difference is largely the result of greater photodegradation at Fort Missoula. Rapid depletion of soil water at both sites limited microbial activity during summer and early fall.

Of the picloram persisting on Day 90, about half was in the first soil stratum, less than a fifth in the second, and a fourth was equally distributed over the next three strata. Of the picloram that persisted at Fort Missoula on Day 90, 75% was equally divided between soil strata 1 and 2, and 22% was in stratum 3. The North Fork vegetation accounted for 9% of the Day 90 pool, while only 2% of the Day 90 pool was in Fort Missoula vegetation.

The rate of loss of picloram from the North Fork (soil plus vegetation) decreased from 0.022 over Day 0 to 7 to 0.0028 for Day 0 through 90. Once within the soil, picloram decayed more slowly because of less favorable microbial conditions than at the valley bottom site.

Stream and Groundwater Studies

The stream was sampled from Day 0 to 90 in response to eight rain events (66 mm in total) that produced measurable increases in stream flow, including 3 mm of rain on Day 2 that caused the largest increase. Stream discharge at the flume varied from 815 to 102 m^3/h while depth to groundwater varied from 0.9 m in June to 2.7 m by September. Leaching of picloram below 75 cm by Day 7 suggests that some picloram may have reached groundwater during the first week; however, analyses never confirmed the presence of picloram in stream discharge or groundwater.

As with most herbicides (Wauchope and Leonard, 1980), the largest reported delivery ratios of picloram from application site to surface waters have been observed with precipitation events that produced overland flow. Picloram movement off the application site has been as high as 5.5 to 6.3% of the applied herbicide (Trichell et al., 1968; Mayeux et al., 1984). In these two studies the combinations of slowly permeable soils, topography, high rainfall intensity, and the treatment of the entire watershed exceed reasonable worst case scenarios for roadside treatment under label restrictions (Date Code B486) in the northern Rockies.

Losses from sites where infiltration is the main hydrological route are lower than those from sites where overland flow is important. Davis and Ingebo (1973) have reported the highest delivery ratios for such watersheds. They treated 0.85 ha of an 18.6 ha Arizona chaparral watershed with pellets at a rate of 10.4 kg picloram/ha. The soil was a gravelly loamy sand with moderately rapid permeability. Total loss was <4.5% and was spread over 413 d. The highest single loss of 0.04%/d occurred with a 6.3-cm rainfall 8 d after application.

Neary et al. (1985) measured picloram fluxes in a North Carolina watershed with high rainfall (205 cm/yr) and rapidly permeable loam soils. Forty percent of a 10-ha watershed was treated with pellets at 5 kg picloram/ha. Three percent of the initial application leached below 1.2 m; however, only trace amounts of picloram were detected in the springs and stream

draining the site. Johnsen (1980) measured a 1.1% loss of picloram from an Arizona pinyon-juniper site when 2.8 kg/ha was applied to 78% of a watershed with shallow (<112 cm), very stoney clay soil with deep surface cracks over impervious bedrock. These large scale applications and environmental conditions represent extreme conditions for offsite transport of picloram by infiltration.

Watershed Detection Limit

The absence of detectable picloram in stream or groundwater during this study does not mean that no picloram reached these waters but rather that any reaching these waters was diluted below the analytical detection limit (0.5 mg/m^3). How much of an application must reach a stream to be detected given the dilution volume associated with various delivery scenarios? The portion that would be detectable is the detection limit of the watershed for a given application. This detection limit may be estimated from the following equation:

$$DR = (DV \times ADL / AP) \times 100\%$$

where DR is the lowest delivery ratio (percent of the application that reaches surface water) causing detectable picloram in surface water, DV is the dilution volume (m^3) of the surface water over the time the substance is likely to be delivered to surface water, ADL is the analytical detection limit of the substance (mg/m^3), and AP is the total pool applied (mg).

The North Fork stream flow varied from 815 to 306 m^3/h over the 6 d following the 3-mm rainfall on Day 2. Given the characteristics of picloram and the saturated soils, most of the herbicide that would move off the site would have done so with this first rain event. The dilution volume for the 24 h following the rainfall (when stream flow was greatest) was 20 000 m^3; the volume was 81 000 m^3 over the 6 d required for the stream to return to baseflow. The watershed detection limit was estimated to be 0.3% (10 g) of the 3 kg application based on the dilution volume of a 1-d period of delivery, or 1.3% (40 g) of the application based on the volume associated with 6 d of delivery. If the herbicide was delivered over <1 d, delivery of even <0.3% could have been detected. Conversely, if delivery occurred over more than 6 d, the loss could have been >1.3% without being detected.

If a rainstorm heavier than 3 mm had occurred, more picloram might have reached the stream; however, the greater flows would raise the dilution volume and the detection limit of the watershed. A very small percent of the watershed was treated in this study, and applications to a larger fraction of a watershed may have delivery ratios that are quite different.

Picloram Dissipation Rates

Loss rates at both sites declined with time. The decay rate at the valley bottom site, which was studied for a longer period, became asymptotic during the second year. Wheatley (1973) noted that residues of many organic chemicals often decline rapidly for a brief period, but the loss rate itself gradually declines. As the soil pool decreases, a larger portion of the residual is held in micropore binding sites not readily available to soil microbes. In climatic zones with strong seasonal patterns, soil drying and freezing arrest biodecay. Residues usually persist longer than would be predicted from the first order kinetics based on a short-term assessment of loss rates. When predicting persistence of picloram, loss rates used must be appropriate in time frame and geographic location.

The rapid initial loss rates in this study were largely a result of photodecay at the soil surface and fall among the lower values for picloram dissipation at the soil surface (Nash, 1980). These rates hold only for short times under similar conditions. The slower loss rates through Days 90, 365, and 455 represent a mixture of loss processes and fall among the lower rates for bulk soils (Nash, 1980).

CONCLUSIONS

An application of 0.28 kg/ha of picloram to a valley bottom site with good herbicide retention characteristics decayed to 56% after 7 d, 36% after 90 d, 13% after 1 yr, and 10.5% after 1.25 yr. The 44% loss during the first week was attributable to photodecay that was the dominant dissipation process during the first growing season. Picloram residues were not detected below a soil depth of 50 cm, and all losses were a result of on-site breakdown. On a mountain logging road with poorer retention and decay characteristics, 86% of a 1.12 kg/ha application was still present after 7 d and 78% persisted after 90 d. Photodecay was less important because of more shade and because rainfall occurred shortly after application to water saturated soils. Picloram was leached to the maximum depth sampled (1 m) within a week. Although the water table was within 1 m of the soil surface at some points between the spray zone and the stream, no herbicide was detected in streamflow nor groundwater.

Most off site loss via infiltration and/or surface flow should have occurred during the 24 h following the first storm after spraying. The dilution capacity from increased streamflow following this storm could absorb 0.010 kg or 0.3% of the application without detection. Any picloram leaving the mountain watershed was at a concentration below the analytic detection limit (0.5 mg/m^3), well below levels causing detrimental effects on beneficial uses of water (e.g., irrigation, aquatic life).

The Tordon 22K (Dow, Midland, MI) label cautions "Do not apply where surface water from treated areas can run off—into streams, irrigation ditches, irrigation ponds, or wells." Roadside ditches discharging directly into streams could transport picloram into surface waters if sufficient rains follow the application. Applications made within label restrictions to water saturated soils could be leached into groundwater and eventually into streams if heavy rains occur before evapotranspiration lowers soil moisture content below what could produce significant capillary flow. However, for roadside treatments in the northern Rockies, if application rates do not exceed 0.28 kg/ha and only a small portion of the watershed is treated (<1% as in this study), stream flow volume following such storms should dilute any picloram moved into streams below established thresholds for harmful effects.

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